

IMOS underway CO₂ dataset report

Dataset: AA2014_068-109_V6 fCO₂ IMOS.txt

Voyage Information:

MV *Aurora Australis* voyage AA1314V6

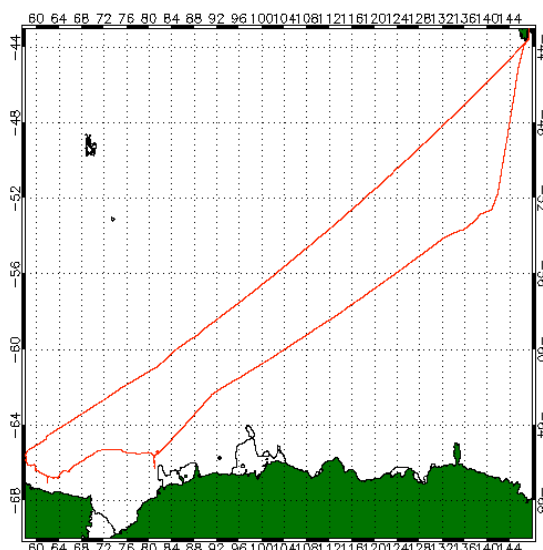
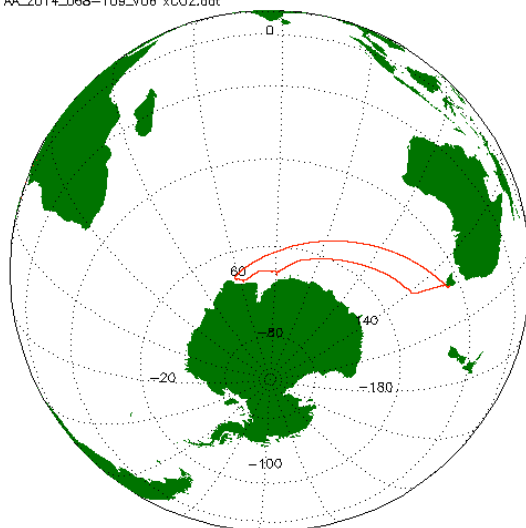
Departed:	Hobart, Tasmania,	March 09, 2014
Arrived:	Hobart, Tasmania,	April 19, 2014

Principal Investigator:

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Track:

AA_2014_068-109_V06_xCO2.dat



Ship Details:

Name: *Aurora Australis*
Call Sign: VNAA
Home Port: Hobart, Australia
Ship owner: P&O Polar

Citation

Publications that use these data should reference the data source as:

Tilbrook, B., C. Neill and J. Akl (2014) Integrated Marine Observing System underway CO₂ data for *Aurora Australis* voyage AA1314V6, <http://www.imos.org.au>.

CO₂ System Overview:

The fugacity of carbon dioxide ($f\text{CO}_2$) in surface seawater was measured using a General Oceanics Inc. automated system (Model 8050; Pierrot *et al* 2009). Seawater is sprayed into an equilibration chamber and CO₂ in the headspace gas equilibrates with the seawater. The headspace gas is pumped through a thermoelectric condenser followed by a nafion drying tube, before flowing through a Licor 7000 non-dispersive infrared gas analyser used to measure the CO₂ mole fraction ($X\text{CO}_2$) of the dried air. The gas flow is stopped temporarily for the CO₂ measurements, which are made at atmospheric pressure. A set of four CO₂ standards (Table 1) that cover the range of CO₂ values expected in the ocean are analysed about every three hours to calibrate the gas analyser. Atmospheric $X\text{CO}_2$ (dry) is measured after the standards by pumping clean outside air from an intake on the forward mast of the ship.

Table 1. CO₂-in-air standard values measured on the WMO-X2007 mole fraction scale

Cylinder no.	Cylinder number	CO ₂ (ppm)
1	CA06898	0.0
2	CA01610	299.41
3	CA01669	353.01
4	CA01673	402.15

Seawater intake and ancillary data

The seawater intake is at about 6 m depth. A remote temperature sensor (Seabird Electronics SBE38) located at the intake is used to measure sea surface temperature (SST). Sea surface salinity is measured using a thermosalinograph (Seabird Electronics SBE21) mounted in the oceanographic lab next to the $p\text{CO}_2$ system. The travel time between the intake and CO₂ system is typically about 70 seconds with warming usually less than 0.7°C in cold waters near freezing. The thermosalinograph water is from the same intake and supply line. Meteorological data, salinity, SST, and ships position and time are taken from the ship's logging system.

System Description:

<i>Equilibrator:</i>	Showerhead, water volume of ~0.5 L, headspace ~ 0.8 L.
<i>Water flow rate:</i>	2 to 3.0 l/min
<i>Headspace gas flow rate:</i>	60-120 ml/min
<i>Measurement method:</i>	Infrared absorption of dried gas.
<i>CO₂ Sensor:</i>	Licor 7000, Serial # IRG4-0910
<i>Resolution/Uncertainty:</i>	±0.3 µatm for equilibrator and atmospheric $f\text{CO}_2$
<i>Equilibrator temperature:</i>	Hart 1521 thermometer (S/N A8B266), 5610-9 probe (S/N B0727114), accuracy ± 0.01°C.
<i>Equilibrator pressure:</i>	Setra Model 239 (S/N 2223344), accuracy ± 0.15 hPa.
<i>Atmospheric pressure:</i>	Druck RPT350 (S/N 2729757), accuracy ± 0.15 hPa. calibrated annually against Druck DPI141 barometric sensor and Bureau of Meteorology barometric pressure standard.
<i>Sea Surface Temperature:</i>	Seabird SBE38, accuracy ± 0.01°C.
<i>Salinity:</i>	Seabird SBE 21 thermosalinograph mounted in the oceanographic lab next to the $p\text{CO}_2$ system, accuracy ±0.01.

Data Fields and Units:

<i>Field</i>	<i>Name</i>	<i>Unit</i>	<i>Description</i>
1.	Group/ship	-	CSIRO/Astrolabe
2.	CruiseID	AAyYyV#	Cruise designation
3.	JD_GMT	ddd.hhhh	Decimal day and time of year, GMT time
4.	Date	yyyymmdd	20111231
5.	Time	hh:mm:ss	UTC time
6.	Lat	degrees	Latitude, decimal degrees
7.	Long	degrees	Longitude, decimal degrees
8.	xCO2EQ_PPM	ppm	Mole fraction of CO ₂ in the equilibrator head space (dry).
9.	xCO2ATM_PPM	ppm	Mole fraction of CO ₂ in the atmosphere (dry) measured every 4 hours after standard runs
10.	xCO2ATM_PPM_INTERPOLATED	ppm	Mole fraction of CO ₂ in the atmosphere (dry) measured every 4 hours after standard runs and values linearly interpolated to the times shown
11.	Press_Equil	hPa	Equilibrator head space pressure
12.	Press_ATM	hPa	Barometric pressure
13.	TEQ	°C	Equilibrator water temperature
14.	SST	°C	Sea surface temperature
15.	SAL	psu	Sea surface salinity
16.	fCO2SW_UATM	µatm	Fugacity of carbon dioxide at surface water salinity and temperature
17.	fCO2ATM_UATM_INTERPOLATED	µatm	fugacity of CO ₂ in the atmosphere
18.	DfCO2	µatm	fCO ₂ SW - fCO ₂ ATM
19.	LICORflow	ml/min	Gas flow through infrared gas analyser
20.	H2Oflow	lpm	Water flow to equilibrator
21.	WindSpd_True	m/s	Wind speed.
22.	WindDirn_True	degrees	Wind direction, 0 is North and 90 is East.
23.	Type	-	Measurement type (equilibrator, standard or atmosphere)
24.	WOCE_QC_FLAG	-	2 = Good 3 = Questionable 4 = Bad (data identified as bad are not reported).

25.	SUBFLAG	-	<p>Secondary flags, only for questionable measurements, WOCE flag 3 (Pierrot <i>et al</i> 2009):</p> <p>1 = Outside of standard range 2 = Questionable/interpolated SST 3 = Questionable EQU temperature 4 = Anomalous (EQU T-SST)($\pm 0.6^{\circ}\text{C}$) 5 = Questionable sea-surface salinity 6 = Questionable pressure 7 = Low EQU gas flow 8 = Questionable air value 10 = Other, water flow</p>
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Quality control and data reduction:

Parameters logged by the fCO₂ system and ship sensors are quality controlled after each voyage.

1. Data with missing parameters or obvious outliers for the ship or fCO₂ system parameters are marked as missing and removed from the calculations. Parameter values are flagged as good (flag=2), questionable (flag=3), or bad (flag=4), depending on the range of values expected. Many of the ship and CO₂ system parameters are not reported in the final dataset, but are used to establish that the system is functioning correctly. For example, water flow rates to the equilibrator below 2 LPM are flagged as questionable and the cause investigated with the flag value changed to 4 if the flow has been interrupted or is insufficient. Similar checks are made to ensure the gas flow through the infrared gas analyser is in a suitable range (50 to 120ml/min). The list of parameters checked are:

CO₂ system data quality controlled:

- GPS date and Time
- Latitude and Longitude
- Water flow rate
- Gas flow rates through licor analyser
- Atmospheric pressure
- Equilibrator pressure
- Equilibrator water temperature
- Mole fraction CO₂
- Water vapour in gas stream
- Licor NDIR temperature

Ship's data quality controlled:

- GPS date and time
- Latitude and Longitude
- Sea surface temperature
- Sea surface salinity
- Relative wind speed and direction
- True wind speed and direction

2. The data sets are next evaluated for excessive warming of the seawater flowing to the equilibrator, and for contamination of the atmospheric measurements by ship stack gas.

The fCO₂ value in the water is sensitive to warming between the ship intake and equilibrator. The travel time between the ship intake and equilibrator is first

checked by comparing the timing of rapid changes in surface water temperature for the intake (SST) and the equilibrator temperatures. The travel time or lag time is normally about 70 seconds. The warming in the system used on MV *Aurora Australis* is typically about 0.4 °C, increasing to about 0.6°C in cooler regions.

Atmospheric CO₂ values can be influenced by contamination from ship stack gas. The atmospheric air intake is located on the Port side above the wheelhouse to collect air in the front part of the ship within about 20m of the ship stacks. The relative wind speed and direction recorded by the ship meteorological sensors are used to if anomalous atmospheric measurements could be due to stack gas contamination. Data where wind speeds are above 3ms⁻¹ and with a direction of ±60° of the bow are typically good values. Data with likely stack gas contamination are flagged as bad (flag = 4) and not included in the calculations outlined below.

3. After completion of the quality control checks, the measured mole fractions are corrected to final values using measurements of the four CO₂-in-air standards (Table 1). The standards are run about every four hours to bracket the air and equilibrator measurements. The offsets between the measured and certified values of each standard are linearly interpolated to the times of measurement of the air and equilibrator samples. At each measurement time, a linear regression of offset values versus certified standard values is used to calculate the offset to apply to the measured air and equilibrator values. The corrections are typically small (less than 1 ppm) and account for drift of the gas analyser response over time. The corrected mole fractions (dry) for the equilibrator and air samples flagged as good are then used to calculate the fugacity of CO₂. Only data flagged as good or suspect are reported in the final data set.

fCO₂SW and fCO₂ATM:

The fugacity of carbon dioxide in seawater is determined using the following equation (Weiss, 1974; Dickson *et al*, 2007):

$$f\text{CO}_{2\text{eq}} = X\text{CO}_2(P_{\text{eq}} - p\text{H}_2\text{O})\exp(P_{\text{eq}}(B + 2\delta)/(R \cdot T_{\text{eq}}))$$

where XCO₂ is the mole fraction (dry) in the equilibrator headspace, P is the pressure in the equilibrator and pH₂O is the water vapour pressure (Weiss and Price, 1980) at the temperature of water in the equilibrator (T_{eq}) and its salinity:

$$p\text{H}_2\text{O}(\text{atm}) = \exp(24.4543 - 67.4509(100/T_{\text{eq}}) - 4.8489\ln(T_{\text{eq}}/100) - 0.000544S)$$

R the ideal gas constant (82.0578 cm³·atm/K·mol), B the virial coefficient of pure CO₂, and the cross virial coefficient of a CO₂-air mixture (Weiss, 1974).

$$B(\text{cm}^3/\text{mol}) = -1636.75 + 12.0408T_{\text{eq}} - 0.032795T_{\text{eq}}^2 + 0.0000316528T_{\text{eq}}^3$$

$$\delta(\text{cm}^3/\text{mol}) = 57.7 - 0.118T_{\text{eq}}$$

An empirical correction (Copin-Montegut, 1988) is applied to account for warming of water between the sea surface and equilibrator. The same equations are applied to the measurements of the mole fraction of CO₂ in atmospheric gas, using the sea surface temperature and atmospheric pressure.

The air-sea gradient in fCO₂ is calculated as: DfCO₂ = fCO₂SW - fCO₂ATM where fCO₂SW is the bulk surface seawater value and fCO₂ATM the atmospheric value.

Processing Comments:

The ship's underway thermosalinograph (salinity), sea surface temperature and meteorological data were collected and calibrated by the Australian Antarctic Division Data Centre.

The time lag between the intake temperature and the equilibrator temperature on this cruise is of less than 70 seconds. This time lag was not applied to the SST data.

While the ship was in heavy ice between 19/03/14 10:16:41 and 27/03/14 16:21:41 several records were flagged as 'bad' and excluded due to insufficient seawater flowing to the $p\text{CO}_2$ system and/or unreliable salinity.

Acknowledgements:

SOOP- CO_2 data was sourced as part of the Integrated Marine Observing System (IMOS) – supported by the Australian Government through the National Collaborative Research Infrastructure Strategy and the Super Science Initiative. Graeme Snow (Australian Antarctic Division) helped run the $p\text{CO}_2$ system during this cruise.

References

Copin-Montegut, C. (1988) A new formula for the effect of temperature on the partial pressure of CO_2 in sea water, *Marine Chemistry*, 25, p29-37 (incl. Corrigendum, *Marine Chemistry* (1989) 27, pp143-144).

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